DEVELOPMENT OF MAGNETIC SUSCEPTIBILITY IN MANGANESE STEEL BY PROLONGED HEAT TREATMENT.

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(*Read April 19, 1918.*)

During the past three years I have had the honor of presenting several papers on "Spontaneous generation of heat in recently hardened steel,"[1] showing that all the specimens treated spontaneously generated heat in easily measurable quantity after hardening by quenching in water at various temperatures above the critical temperature of decalescence. Carbon tool steel, "high-speed" tungsten-chromium steel, and several specimens of nickel-chromium steel were tested. In all cases the generation of heat was most pronounced immediately after quenching and diminished rapidly, though it continued observable a week or more. Generation of heat was always conditional on true hardening, by quenching at a temperature above the critical point, except in the case of one of the nickel-chromium specimens. Here moderate, but unequivocal, generation of heat followed quenching at a temperature just *below* the critical point, reached by *falling* slowly from a higher temperature through full recalescence. While true hardening could not have occurred, yet there was a well-marked "stiffening" or incipient hardening of the metal as shown by subsequent hardness tests. When, however, the same steel, after annealing, was slowly *raised* to the same temperature (but not above) and quenched, no generation of heat followed. In this connection another interesting phenomenon developed as follows: When the same lot of nickel-chromium steel, after annealing, was quenched at several successively higher (rising) temperatures, but all below the critical temperature,

[1] *Proc. Am. Phil. Soc.*, Vol. LIV., No. 217, May–July, 1915. *Phys. Review*, N. S., Vol. IX., No. 3, March, 1917. *Proc. Royal Soc.*, Series *A*, Vol. 93, No. *A*, 649, Apl. 2, 1917. Joint paper with Sir Robert Hadfield. *Proc. Am. Phil. Soc.*, Vol. LIV., No. 4, 1917.

each quenching was followed by a small but distinct *absorption* of heat.

The phenomena above outlined appear to be new, and have aroused the interest of some eminent metallurgists, among others Sir Robert A. Hadfield, who kindly furnished all the specimens of nickel-chromium steel employed, and to whom I am greatly indebted for joining in some of the later work, and incidentally confirming the most important of my findings with different apparatus of his own design.

The foregoing outline of former work is introduced here because it underlies, and is closely associated with, the subject matter of the present paper.

Sir Robert Hadfield long ago suggested that interesting results might follow similar experiments with manganese alloy-steel (with which his name is so intimately connected).

As is well known, this remarkable steel is exceedingly tough, and difficult to work with machine tools though not hard; its softest and toughest condition is brought about by water-quenching at a high temperature, after which it is almost completely non-magnetic; it has no critical temperature, and hence cannot be hardened in the ordinary sense; when heated a long time at a moderate temperature it becomes magnetic, loses much of its tensile strength, and all its toughness, and becomes brittle and considerably harder.

For the purposes of the following experiments Sir Robert Hadfield sent me 19 numbered bars of his manganese steel, each 6 inches long and ½ inch in diameter (round), all cut from the same long bar and ground to size after treatment.

Following is his specification:

Analysis.—C, 1.18 per cent.; Si, .14 per cent.; Mn, 12.29 per cent.

Bars 1 to 6, As forged. Non-magnetic.

Bars 7 to 12, Toughened by water-quenching at 995° C. Non-magnetic.

Bars 13 to 18, Toughened as above, then reheated to 500° and kept at that temperature 63 hours. Magnetic.

Bar 19, Treated like 13 to 18, then reheated to 995° and water-quenched. Non-magnetic.

I carefully tested one bar of each description for scleroscope hardness, with following results:
Bar No. 1 (as forged). Hardness 37.3.
Bar No. 7 (toughened). Hardness 28.5.
Bar No. 15 (toughened, reheated). Hardness 51.6.
Bar No. 19 (toughened, reheated, retoughened). Hardness 39.

Each of the above hardness numbers (and those to follow) is the mean of at least ten consistent measurements made on the carefully ground, horizontal end surface of the bar, a fresh spot being used for each measurement.

I subsequently heated bar No. 13 to 1074° and cooled (annealed) in the furnace. Its hardness, which presumably had been about 51.6 like its companion No. 15, was then 28.8, and it was non-magnetic; seeming to show that quenching at high temperature, and annealing from a still higher temperature, gives the same hardness and non-magnetic condition whatever previous treatment may have been. The hardness of bar No. 19 seems to contradict this conclusion, in respect of hardness, but it was quenched at a very considerably lower temperature.

In the following experiments ten of the 6-inch bars of manganese steel were used, so as to approximately equal in weight the twelve 5-inch bars of other steels employed in former experiments.

First quenching: Bars 1 to 5 and 7 to 11 (10 in all) were heated in an electric muffle furnace to 1013° C. and quenched in water. This treatment was followed by no appreciable generation or absorption of heat when tested in the calorimeter employed in former experiments and described in the earlier papers referred to.

Hardness was now: Bar No. 1, 30; Bar No. 7, 28.3, showing that the first lot "as forged" and the second lot "toughened" were brought to substantially the same "toughened" condition.

Second quenching: The ten bars were again heated to 1013°, allowed to cool in the furnace to 800° and quenched. Again there followed no appreciable generation or absorption of heat.

Hardness was now: Bar No. 1, 27.6; Bar No. 7, 26.3.

Third quenching: The bars were heated to 818°, allowed to cool in the furnace to 607°, and quenched. There was no subsequent generation or absorption of heat.

Hardness was: Bar No. 1, 26.3; Bar No. 7, 26.6.

The ten bars were next heated slowly to 645° and allowed to cool slowly in the furnace to room temperature.

Hardness was: Bar No. 1, 26.5; Bar No. 7, 25.9.

All the bars were now very moderately magnetic, though in their softest condition.

The foregoing quenching temperatures were *falling* ones. The following quenching temperature was a *rising* one, from the annealed condition last described.

Fourth quenching: The bars were heated slowly to 615° and quenched.

Hardness was now: Bar No. 1, 38; Bar No. 7, 30.3.

Notwithstanding this considerable increase of hardness, there followed no appreciable generation or absorption of heat. The bars remained very moderately magnetic.

The results of the foregoing experiments make it highly probable that no spontaneous generation or absorption of heat can be brought about by quenching this manganese steel at any temperature, rising or falling, while in its normal, useful non-magnetic condition. But it was thought worth while to make further experiments with the steel in its magnetic condition and, incidentally, to study the development of this magnetic condition during the prolonged moderate heating necessary to bring it about. The latter study has proved so interesting that I have pursued it to considerable length and made it the titular subject of this paper.

The apparatus employed in the following study consists, in part, of a vertical cylindrical electric furnace heated by small spirals of "nichrome" wire carrying alternating current regulated by a rheostat. The heating spirals are so disposed as not to produce any magnetic field inside or outside the furnace. Instead of the usual sheet-iron casing, this furnace is cased with sheet brass slotted longitudinally to prevent induction currents in it when the external magnetizing solenoid is excited. The furnace is surrounded by a solenoid 16 inches inside, and 20 inches outside diameter, and 4 inches long (high), consisting of 860 turns of No. 12 insulated copper wire wound in two equal coils adapted to be placed in series or parallel relation by means of a suitable switch. The axes of the furnace and solenoid are coincident. The solenoid is excited by current from a 65-volt storage battery, controlled by a rheostat, and the circuit is closed and opened by a switch which breaks simultaneously at three points in series, so as to avoid the destructive arc which would occur at a single break. An ammeter and reversing switch are included in the line.

A single turn of asbestos-insulated platinum wire is located in the furnace, and the ends of this loop are connected by a twisted cable with a ballistic mirror-galvanometer of 600 ohms' resistance.

When the solenoid circuit is closed, a brief electric current is induced in the platinum loop in the furnace and causes a minimum swing of the galvanometer scale easily read with considerable precision.

When a bundle of ordinary steel or iron bars is placed within the platinum loop the galvanometer deflection is, of course, many times greater, and is fairly proportional to their magnetic susceptibility, after deducting the minimum deflection due to the platinum loop alone, and when the excitation of the solenoid is not too small or too great. In the following experiments with the manganese steel, 9 amperes was found to ba suitable exciting current with the solenoid coils in series. Small variations of exciting current were reduced to this value in computing results. Residual magnetism was measured by the usual method of reversals, and allowed for.

The above described apparatus was originally designed and constructed for a rough study of the magnetic properties of metals and alloys at temperatures up to and above their melting points, and has proved very useful. A high-temperature furnace with slotted brass casing is included in the general outfit.

Preparatory to the following study of magnetic susceptibility of the manganese steel brought about by prolonged heating, ten half inch round bars, 6″ long, of Swedish charcoal iron were placed within the platinum loop in the furnace, and the galvanometer deflection was repeatedly observed when the solenoid was excited by various amounts of current. Nine amperes was found to give conveniently large deflection, which was closely proportional to the current through a wide range about this value. This condition was also found approximately true when the manganese steel bars, made magnetic by heating, were subsequently substituted for the charcoal iron.

In the following experiments galvanometer deflection, less that amount due to the platinum loop alone, is taken as the measure of magnetic susceptibility, and the susceptibility of the Swedish iron is used as a standard and assigned a value of 100. All other values are reduced to and expressed in terms of this standard.

As a preparatory measure, the ten bars of manganese steel were brought to their softest and toughest condition by quenching at 1000°.

Hardness was: Bar No. 1, 26.7; Bar No. 7, 25.8.

All the bars were quite free from any trace of magnetism.

The bars were next placed within the platinum loop in the electric furnace and heated 170 hours to a temperature fluctuating between 505° and 525°. The growth of magnetic susceptibility is plotted in the curve shown in Fig. 1. There is no doubt that the

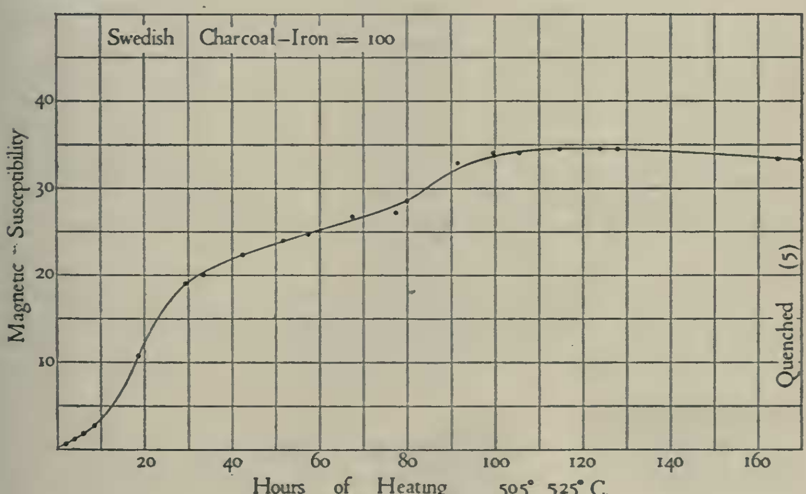

FIG. 1.

curve would have been smoother if the temperature had remained constant. It was intended to use about 515° temperature, and it was held near that value by the rheostat during the first few hours Subsequent fluctuations were due to variations of voltage in the alternating heating current. The higher temperatures usually occurred in the latter part of the night, and were always accompanied by more than average rise of susceptibility. But the large depression in the central part of the curve is thought to be due to some obscure cause, and not to temperature variation.

The entire absence of growth of susceptibility during the last 50 or more hours prompted the belief that the steel had reached a stable condition at the temperature of treatment, and led to the discontinuance of this experiment. Permanent magnetism, which had been considerable while susceptibility was rising, fell off very much during the last two or three days.

Fifth quenching: At the end of 170 hours the bars were quenched, after which they exhibited moderate, but typical and unequivocal generation of heat.

Hardness was: Bar No. 1, 48.1; Bar No. 7, 47.2.

This great increase of hardness (from 26.7 and 25.8 in the annealed condition) brought about by the long heating, doubtless accounts for the spontaneous generation of heat observed.

During the long heating the bars acquired a rather thick coating of black oxide which peeled off almost completely in quenching, leaving clean metal surface. The oxide was strongly magnetic; but its weight was so small, compared with the total weight of the bars, that it could not have affected, materially, the foregoing magnetic observations.

The bars were again placed in the furnace and heated to a higher temperature than before, fluctuating between 590° and 598°, for the first 90 hours (from 170 to 260 hours, reckoned from beginning of treatment).

The results of this procedure are plotted in the first curve of Fig. 2. It is seen that magnetic susceptibility started at a very considerably higher value than it had at the end of the previous treatment. The reason of this increase during the intervening few days, without heating, is not clear. It may have occurred at the moment of quenching; or, more likely, during the period of spontaneous heat generation which followed the quenching.

The curve shows a very regular, but steadily diminishing, growth of susceptibility at this higher temperature, until it reaches nearly double the value it had at the end of the previous treatment.

Fig. 2 shows that at the 260-hour point of total treatment the temperature was quickly raised about 25°, *i. e.*, to 619°, and continued at that point about ten hours. This moderate rise in temperature brought about a sudden and very considerable fall in susceptibility, approaching stability at the end of the ten hours.

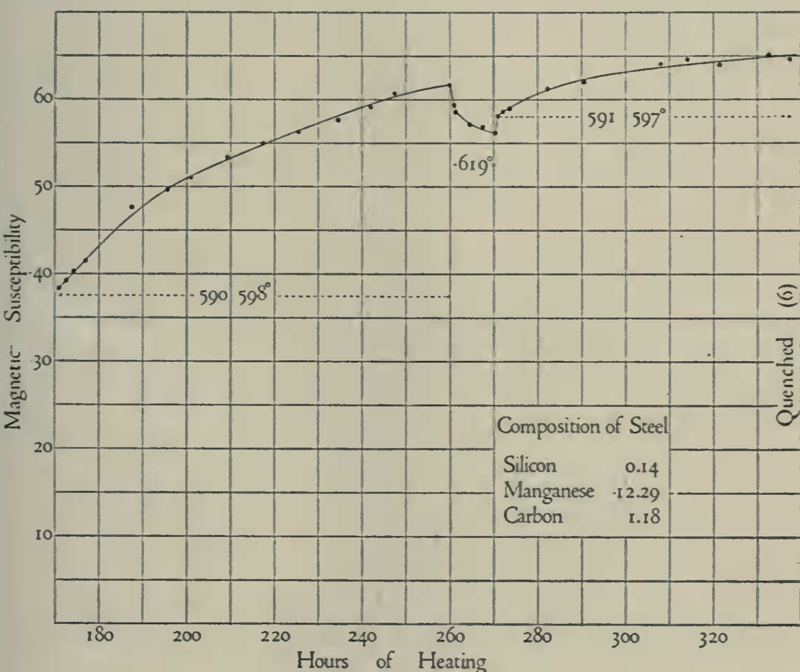

FIG. 2.

When the temperature was next quickly lowered to its former value and then continued to the end of the experiment, 175 hours (340 hours total), there was at first a sudden rise of susceptibility, followed by steady growth as before. All these changes are clearly shown in Fig. 2.

Great sensitiveness to temperature change is indicated at about 600°.

Sixth quenching: At the end of 344 hours, total, of treatment, the bars were again quenched. This was followed by very little, if any, spontaneous generation of heat.

Hardness was: Bar No. 1, 37.4; Bar No. 7, 36.2.

This shows a very considerable softening since the last quenching, notwithstanding the large increase of magnetic susceptibility. The softening may account for the absence of heat generation after the quenching.

The magnetic susceptibility of the cold quenched bars was almost the same (slightly lower) as before quenching.

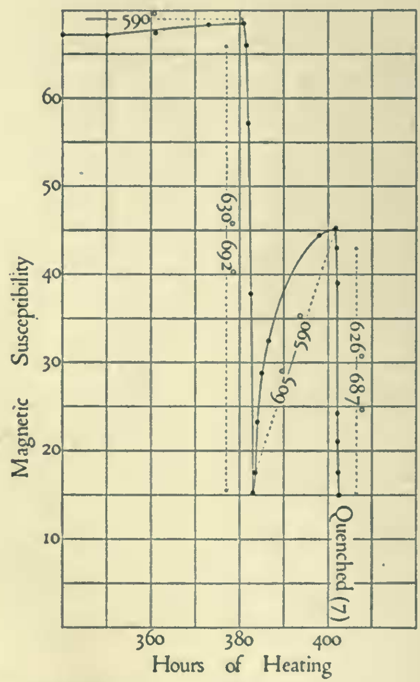

FIG. 3.

The ten bars were again heated, slowly this time, to 590° and held nearly at that temperature until the 381st hour of total treatment, as shown in Fig. 3. Susceptibility rose slightly, reaching its highest value, 68.5. As this is comparable with the susceptibility of ordinary steel, the manganese had apparently almost completely lost its influence.

At this stage it was thought that decalescence might possibly be brought about by cautiously raising the temperature, and the effect of doing so is shown in the great and nearly vertical drop in the susceptibilty curve. The stations in this part of the curve represent observations at half-hour intervals, indicating two hours for the total drop, with the temperature steadily rising to the maximum of 692°.

It seemed clear that decalescence was not taking place, because loss of susceptibility was far too slow in time, and the maximum temperature reached was not sufficiently high. Probably the manganese was simply resuming its sway.

The temperature was next rapidly lowered to 605°–590°, bringing on a rapid recovery of magnetic susceptibility, amounting to 30 points in 21 hours as shown.

Again the temperature was raised, but much more rapidly than before, resulting in a much steeper drop in the curve, the observation stations shown representing only five-minute intervals.

Seventh quenching: At the end of the curve shown in Fig. 3 the steel bars were quenched at 687°. Subsequently there was no trace of generation or absorption of heat. Hence it is virtually certain there had been no decalescence.

Hardness was: Bar No. 1, 42; Bar No. 7, 41.8.

Sir Robert Hadfield long ago assured me that the study of manganese steel is full of surprises for the investigator. I have experienced some of them, and hesitate at present to draw definite conclusions from the results of the experiments just described. The manner in which the manganese operates in completely obliterating the magnetic quality of seven times its weight of iron is, so far as I am aware, not yet known; and the instability of the alloy or, probably, mixture of alloys, in which the carbon present may play an important part, at about 600° temperature as herein shown, is most remarkable and promises a fertile field for future investigation.

I am contemplating the study of a similar ferro-manganese alloy free from carbon.

Cleveland, O.,
April, 1918.